

## PATENT ABSTRACTS OF JAPAN

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## (54) COMPOSITION FOR IMPROVEMENT OF PAPER SURFACE QUALITY

## (57)Abstract:

PURPOSE: To obtain the subject composition capable of improving infiltration of a sizing agent such as starch into paper, paper strength and light resistance without generating unevenness of coating by blending a specified acrylamide-based resin with starch, etc.

CONSTITUTION: This composition for improvement of paper surface quality is obtained by blending (A) 5 to 90wt.% polyacrylamide-based resin synthesized by polymerizing monomers essentially composed of (A1): an acrylamide and (A2): one kind of vinyl monomer selected from an  $\alpha$ ,  $\beta$ -unsaturated monocarboxylic acid, an  $\alpha$ ,  $\beta$ -unsaturated dicarboxylic acid, an  $\alpha$ ,  $\beta$ -unsaturated tricarboxylic acid, an unsaturated sulfonic acid and their salts in the presence of urea with (B) 10 to 95wt.% one or more kinds of substances selected from water soluble polymers of starch, a starch derivative (oxidized starch), a cellulose derivative (CMC) and PVA. This surface coating composition is excellent in prevention of unevenness or sticking in coating when applied to paper or paperboard using a Gate roll coater, etc.

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CLAIMS

[Claim(s)]

[Claim 1] Under existence of a urea, (1) Acrylamides (a), alpha, beta partial saturation monocarboxylic acid, alpha, beta partial saturation dicarboxylic acid, alpha, beta partial saturation tricarboxylic acid, a partial saturation sulfonic acid, And the acrylamide system (resin A) 5-90 % of the weight obtained by carrying out the polymerization of at least one sort of vinyl monomers (b) chosen from the group which consists of those salts as an indispensable component, (2) -- the front face characterized by containing one sort chosen from the group of the water soluble polymer of starch and a starch derivative, a cellulosic, and polyvinyl alcohol, or two or more sorts of 10 - 95 % of the weight -- quality of paper -- the constituent for improvement.

[Claim 2] the front face according to claim 1 whose starch derivative is oxidized starch -- quality of paper -- the constituent for improvement.

[Claim 3] the front face according to claim 1 whose cellulosic is a carboxymethyl cellulose -- quality of paper -- the constituent for improvement.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] the front face which this invention excels [ front face ] in the improvement in the surface reinforcement of paper, internal reinforcement, a water resisting property, etc., and discovers the good permeability to Kaminaka -- quality of paper -- it is related with the constituent for improvement.

[0002]

[Description of the Prior Art] Development of a printing technique in recent years is remarkable, and printabilities, such as advanced surface reinforcement, internal reinforcement, and a water resisting property, have come to be required from a print sheet with high-speed-izing of printing, and quality improvement. The chemical for corresponding to these demands is added to the aqueous slurry of pulp, or carrying out coating (outside \*\*) to the front face of (internal) and paper is performed.

[0003] the front face aiming at raising the surface reinforcement of paper and raising a printability -- quality of paper -- conventionally, the water soluble polymer of nature, such as cellulose, such as starch derivatives, such as starch, oxidized starch, cation-ized starch, and oxygen denaturation starch, and a carboxymethyl cellulose (it omits Following CMC), polyvinyl alcohol (it omits Following PVA), and anionic polyacrylamide, or composition is used for the improver, and most oxidized starch is used for it especially. However, since the process which cooks them and is dissolved is required for them in case a starch derivative and a PVA derivative are used, its workability is bad, and there are various problems, such as foaming, at the time of coating.

[0004] Furthermore, the problem of putrefaction and aging is also in starch. As a surface treatment agent of paper, the water-soluble polymer which carried out carboxyl group denaturation by hydrolyzing partially in front after having used together the monomer which has remarkable solubility to water like acrylonitrile etc. to the acrylic acid or the methacrylic-acid pan as acrylamide system resin, and usual having carried out radical copolymerization underwater or carrying out aqueous polymerization of the acrylamide is proposed in order to mainly improve surface reinforcement (JP,43-27529,B).

[0005]

[Problem(s) to be Solved by the Invention] however, the latest advanced front face -- the demand of quality of paper -- receiving -- the aforementioned existing front face -- quality of paper -- in an improver, a still sufficiently satisfactory result is not obtained but the trouble on printing resulting from lack or waterproof lack of the surface reinforcement of paper and internal reinforcement is increasing. The early problem solving is called for especially about the coating unevenness and \*\*\*\*\* which pose a problem when surface coating is carried out by the gate roll coater, meta-ring blade size press, etc. especially -- \*\*\*\*\* -- the front face to Kaminaka -- quality of paper -- the front face which is the problem generated since the permeability of an improver is not enough, and is more excellent in permeability -- quality of paper -- an appearance of an improver was desired. what this invention answers the request -- it is -- the permeability to Kaminaka -- high -- a front face with few coating unevenness and

the problems of \*\*\*\*\* -- quality of paper -- it aims at offering an improver.

[0006]

[Means for Solving the Problem] the acrylamide system resin which carried out the polymerization of the specific vinyl monomer to acrylamides under existence of a urea as a result of inquiring wholeheartedly that this invention person etc. should attain the purpose, and the front face containing starch etc. -- quality of paper -- using the constituent for improvement -- various kinds of front faces -- being able to improve quality of paper with sufficient balance, paper of fine quality finds out demonstrating the effectiveness which was excellent also in the newsprint from the first, and came to complete this invention.

[0007] This invention under existence of ureas Namely, acrylamides (a) alpha, beta partial saturation MONORU carboxylic acid, alpha, beta partial saturation dicarboxylic acid, alpha, beta partial saturation tricarboxylic acid, A partial saturation sulfonic acid and 5 - 90 % of the weight of acrylamide system resin obtained by carrying out the polymerization at least of a kind of vinyl monomer (b) chosen from the group which consists of those salts as an indispensable component, the front face characterized by containing one sort chosen from the group of the water soluble polymer of starch and a starch derivative, a cellulosic, and polyvinyl alcohol, or two or more sorts of 10 - 95 % of the weight -- quality of paper -- the constituent for improvement is offered.

[0008] Next, this invention is explained to a detail. As ureas used by this invention, although a urea, thiourea, an ethylene urea, ethylenetiourea, etc. are mentioned, especially a urea is desirable. as acrylamides, N permutation (meta) acrylamides other than acrylamide and meta-acrylamide, such as N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N, and N-dimethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-octyl (meta) acrylamide, mention -- having -- these -- one sort -- or two or more sorts can be used.

[0009] As alpha, beta partial saturation monocarboxylic acid, and those salts, an acrylic acid, methacrylic acid and those sodium salt, potassium salt, ammonium salt, etc. are mentioned. As alpha, beta partial saturation dicarboxylic acid, and those salts, a maleic acid, a fumaric acid, an itaconic acid, citraconic acids and those sodium salt, potassium salt, and ammonium salt are mentioned. As alpha, beta partial saturation tricarboxylic acid, and those salts, they are aconitic acid, 3-butene-1, 2, 3-tricarboxylic acid, and 4-pentene. - 1, 2, and 4-tricarboxylic acid and those sodium salt, potassium salt, and ammonium salt are mentioned.

[0010] The cationic monomer in which a polymerization like dimethylaminopropyl (meta) acrylamide and the 4th class ghost of its other than these anionic monomers is possible or the styrene of the amount of extent which does not injure the water solubility of resin, the methyl vinyl ether, the alkyl ester of the carbon numbers 1-8 of an acrylic acid (meta), 2-hydroxy ester, or glycidyl ester may be used together as a copolymerization component. <BR> [0011] Otherwise as a cationic monomer, it is 2-hydroxy. - It is N, N, N, N', and N'-pentamethyl. - It is N'. - (3-(meta) acryloyl aminopropyl) -1, 3-propane dianmonium dichloride, 2-hydroxy-N-benzyl-N and N-diethyl - N' and N'-dimethyl - N' - (2-(meta) acryloyloxyethyl) -1, 3-propane dianmonium dibromide, N and N-dimethylaminoethyl (meta) acrylate, N, and N-dimethylaminopropyl (meta) AKURU amide, N-ethyl-N and N-dimethyl (2-(meta) acryloyloxyethyl) ammonium star's picture, N-benzyl-N and N-dimethyl-(3-(meta) acryloyl aminopropyl) ammoniumchloride, a diaryl amine, vinylpyridine, a vinyl imidazole, etc. are mentioned.

[0012] The cross linking agent other than these monomers may be used. As a cross linking agent, the cross linking agent of the arbitration currently conventionally used for polyacrylamide system resin can be used. As an example, ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as propylene glycol (meta) acrylate and TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as hexa methylenebis (meta) acrylamide Epoxy acrylate, a divinylbenzene, urethane acrylate, diallyl phthalate, diallyl maleate, a triaryl SHIANU rate, triallyl isocyanurate, a dimethylolurea, a dimethylol ethylene urea, [0013] In addition, the poly aldehyde compounds, such as the poly methylol compounds, such as the Pori methylolurea, a methylol ethylene urea, a dimethylol glyoxal MONOU lane, dimethylol glyoxal diureine, uronic dimethylol, a dimethylol propylene urea, 1, 3-screw-(hydroxymethyl) tetrahydro-

5-hydroxy-2-pyrimidinone, dimethylol triazon, the poly methylol melamine of a dimethylol melamine and others, and poly methylol ASETOGU Anacin, and glyoxal, glutaraldehyde, and dialdehyde starch, are mentioned.

[0014] The suitable polymerization initiator for the bottom of existence of ureas is used for the polymerization of the acrylamide system resin (A) of this invention, and it is 40-100 degrees C in temperature, and performs the reaction of 1 - 10 hours. The weight ratio of a urea and monomers is 80 - 50% of 20 - 50% pairs preferably 95 - 40% of 5 - 60% pairs. When there are more ureas than this range, or when few, the permeability to Kaminaka, surface reinforcement, internal reinforcement, a water resisting property, etc. cannot be balanced, and it is not desirable.

[0015] What has a well-known polymerization initiator is used. As a radical polymerization initiator, water-soluble catalysts, such as sodium persulfate, potassium persulfate, ammonium persulfate, a hydrogen peroxide, and the second cerium salt, are used 0.01 to 5% of the weight to total monomer weight. Moreover, redox polymerization can also be carried out using reducing agents, such as dimethylamine, a sodium hydrogensulfite, and sodium formaldehyde sulfoxylate. Moreover, a well-known chain transfer agent may be used if needed. As the class, allyl compounds, such as allyl alcohol, allylamine, and sodium allylsulfonate, mercaptoethanol, thioglycolic acid, its alkali-metal salt or ammonium salt, isopropyl alcohol, sodium hypophosphite, etc. are mentioned.

[0016] Acrylamides (a), alpha, beta partial saturation monocarboxylic acid, alpha, beta partial saturation dicarboxylic acid, The weight ratio of alpha, beta partial saturation tricarboxylic acid, a partial saturation sulfonic acid, and at least one sort of vinyl monomers (b) chosen from the group of those salts (a) is 99.5% - 50%, (b) is 0.5 - 50%, (a) is 98% - 85% preferably, and (b) is 2 - 15%.

[0017] As for the water soluble polymer mixed with acrylamide system resin (A), cellulose, such as starch derivatives, such as starch, oxidization starch, and cation-ized starch, and a carboxymethyl cellulose, and polyvinyl alcohol are mentioned. the weight ratio of the water soluble polymer (B) mixed with the acrylamide system resin (A) containing ureas -- (A)/(B) -- 5 - 90%/-- they are 5 - 50% / 95 - 50% preferably 10 to 95%. According to the application of the target paper, the permeability to Kaminaka, surface reinforcement, internal reinforcement, and waterproof balance are considered, and a ratio is selected.

[0018] the front face of the paper of this invention -- quality of paper -- the surface coating liquid containing the constituent for improvement mixes the water solution of acrylamide system resin (A), and the water solution of the above-mentioned water soluble polymer (B), or it can cook after mixing the water solution of acrylamide system resin, and the dispersion liquid of the above-mentioned water soluble polymer, and it can adjust them. Additives, such as a surface sizing compound, a non-skid agent, antiseptics, a defoaming agent, a viscosity controlling agent, and a color, may be used together in the surface coating liquid of this invention. In addition, as for the concentration of coating liquid, it is desirable to be carried out at 0.1 - 15%.

[0019] The approach size press, a gate roll coater, a blade coating machine, or a calender performs the surface coating liquid in connection with this invention for carrying out coating to paper or the paper board is desirable. Moreover, coating can be carried out by the bar coating machine, the knife coating machine, an air knife coater, etc. Moreover, coating of the surface coating liquid in connection with this invention can be carried out to various stencil paper, such as coat stencil paper (acid paper, alkaline paper), a newsprint, a liner, a coat ball, printing writing paper, a form form, a PPC form, inkjet printing paper, and a thermal paper. Although also whenever [ size / of stencil paper ] is arbitrary, when carrying out coating using size press etc., it is desirable to use an internal sizing compound in order to adjust the liquid adsorption of stencil paper.

[0020]

[Example] Hereafter, although an example explains this invention, this invention is not restricted at all by these. In addition, measurement was performed according to the following approach. internal: on the strength -- SUKOTTO bond method; -- the internal bond tester (Kumagaya Riki Kogyo K.K. make) was used, and it measured on the bond strength of 1kg/cm<sup>2</sup>, and the

conditions for 30 seconds.

surface: on the strength -- dry pick; RI printing testing-machine and nip width-of-face ink [ of 10mm ]; FINE INK. (the Dainippon Ink & Chemicals make --) ink for IGT printability trial T.V.= -- 18 or 20 -- wet -- a pick; RI printing testing machine -- nip width of face of 10mm mol ton roll use ink; -- CAPS G (Dainippon Ink & Chemicals make, for offset) ink T.V.= -- 8 or 10.5 -- the paper after printing all turned, the condition was observed with the naked eye, and five-step evaluation was performed by making 1 into \*\*, having made 5 as A.

wax pick; -- JIS P-8129 size whenever: -- Stockigt method; -- JIS P-8122-1976 [0021] In 11. 4 opening flask which attached the example agitator of manufacture, the thermometer, the ring current cooling pipe, and nitrogen gas installation tubing of acrylamide system resin (A), 402.32g of water, 90.89g (a urea is 40% of the weight of the sum total of a urea and a monomer) of ureas, 206.90g (97-mol %) of 50% acrylamide water solutions, 5.85g [ of itaconic acids ] (three-mol %) and 2-propanol 18.03g was taught, subsequently 6.85g of ammonium persulfate water solutions was added 5%, the temperature up was carried out to 80 degrees C under nitrogen gas installation, and it was made to react for 2 hours. 17.58g of ion exchange water was added to the obtained polymer, and the transparent water solution of the solid content of 29.8%, the viscosity of 5100cps, and pH7.10 was obtained. Let this be resin 1.

[0022] the coating liquid (12.7% of concentration and the viscosity in 50 degrees C are 30.5cps) which carried out 5.6 weight sections (solid content) mixing, and obtained the resin 1 of the above-mentioned example of manufacture in the oxidized starch 94.4 weight section (solid content) cooked at 12% of example 1 concentration -- acid paper of fine quality (basis-weight 75 g/m<sup>2</sup>) -- a system gate roll coater (a part for speed 800m/) -- coating -- it dried and coated paper was obtained. In addition, coating temperature was performed at 50 degrees C.

[0023] the coating liquid (13.1% of concentration and the viscosity in 50 degrees C are 33.5cps) which carried out 8.3 weight sections (solid content) mixing, and obtained the resin 1 of the above-mentioned example of manufacture in the oxidized starch 91.7 weight section (solid content) cooked at 12% of example 2 concentration -- the quality of an acid overlay (basis-weight 75 g/m<sup>2</sup>) -- a system gate roll coater (a part for 800m/) -- coating -- it dried and coated paper was obtained. In addition, coating temperature was performed at 50 degrees C.

[0024] the oxidized starch (the viscosity in 50 degrees C is 28.5cps) cooked at 12% of example concentration of a comparison -- acid paper of fine quality (the basis weight of 75g/m<sup>2</sup>) -- a system gate roll coater (a part for 800m/) -- coating -- it dried and coated paper was obtained. In addition, coating temperature was performed at 50 degrees C.

[0025] Paper durability was measured for the coated paper obtained by the evaluation example and the example of a comparison of the test paper after gas conditioning under the conditions of 20 degrees C and 65% relative humidity. In addition, measurement was performed according to the following approach. As the result was shown in Table 1, it was admitted that the direction of the coated paper of an example was excellent in surface reinforcement, such as a wax pick, a dry pick, and a wet pick, the internal reinforcement as which it is indicated with SUKOTTO bond, and size nature. Moreover, it turns out that the coated paper of an example 2 excels the coated paper of an example 1 in dry pick, wet pick, and SUKOTTO bond and the Stockigt size.

[0026] Moreover, the osmosis condition of the starch to Kaminaka was measured using the coated paper by the example 1, the example 2, and the example of a comparison. Measurement exfoliated each coated paper in four layers, and carried out the quantum of the amount of starch of each class by the biosensor method (BF-DP:KS systems incorporated company) (as an amount of glucoses). This was shown in Table 1. Z shaft orientations of coated paper are expressed with % display in front Naka. That is, in 0% of Z shaft orientations, the rear face is expressed as the front face of coated paper, and 100% of Z shaft orientations, and it is shown [% / of Z shaft orientations / 25 ] that it is in 25% of location toward a rear face from the front face at the time of coating (surface approach).

[0027] The coated paper of an example can check a thing with many (starch has permeated) amounts of glucoses on each class of coated paper rather than the example of a comparison. When the paper Nakauchi section (25 - 65% of Z shaft orientations) compares especially, it is clear that many amounts of glucoses are contained in the example to the example of a

comparison. Moreover, as for an example 1, the example 2 shows that there are also many amounts of glucoses of coated paper each class. Although the value of Table 2 is plotted to drawing 1, examples 1 and 2 can check that the glucose (oxidized starch) has permeated the interior of coated paper.

[0028]

[Table 1]

表1 表面強度、内部強度及びサイズ性の測定結果

| 試験項目            | 実施例1 | 実施例2 | 比較例  |
|-----------------|------|------|------|
| ワックスビック         | 18   | 18   | 14   |
| ドライビック          | 4.9  | 5.0  | 4.6  |
| ウェットビック         | 4.8  | 5.0  | 4.4  |
| スコットボンド [g[:cm] | 2.03 | 2.09 | 1.90 |
| ステキヒトサイズ [sec]  | 76.6 | 78.1 | 74.4 |

[0029]

[Table 2]

表2 塗工紙の各Z軸方向におけるグルコース量

| グルコース量 (対紙重量%)       |      |      |      |
|----------------------|------|------|------|
| Z軸方向 (%)             | 実施例1 | 実施例2 | 比較例  |
| 12.4<br>13.2<br>13.5 | 2.05 | 2.21 | 1.75 |
| 27.6<br>33.1<br>43.0 | 0.44 | 0.52 | 0.00 |
| 39.8<br>59.6<br>63.0 | 0.70 | 0.83 | 0.05 |
| 82.7<br>84.1<br>89.3 | 2.43 | 2.67 | 1.26 |

[0030]

[Effect of the Invention] According to this invention, the effectiveness which was excellent in carrying out mixed use of the ureas content polyacrylamide system resin to coating unevenness or \*\*\*\*\* at them since osmosis in Kaminaka of starch, a cellulosic, and polyvinyl alcohol was raised to starch, a cellulosic, and polyvinyl alcohol is demonstrated.

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TECHNICAL FIELD

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[Industrial Application] the front face which this invention excels [ front face ] in the improvement in the surface reinforcement of paper, internal reinforcement, a water resisting property, etc., and discovers the good permeability to Kaminaka -- quality of paper -- it is related with the constituent for improvement.

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PRIOR ART

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[0004] Furthermore, the problem of putrefaction and aging is also in starch. As a surface treatment agent of paper, the water-soluble polymer which carried out carboxyl group denaturation by hydrolyzing partially in front after having used together the monomer which has remarkable solubility to water like acrylonitrile etc. to the acrylic acid or the methacrylic-acid pan as acrylamide system resin, and usual having carried out radical copolymerization underwater or carrying out aqueous polymerization of the acrylamide is proposed in order to mainly improve surface reinforcement (JP,43-27529,B).

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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## MEANS

[Means for Solving the Problem] the acrylamide system resin which carried out the polymerization of the specific vinyl monomer to acrylamides under existence of a urea as a result of inquiring wholeheartedly that this invention person etc. should attain the purpose, and the front face containing starch etc. -- quality of paper -- using the constituent for improvement -- various kinds of front faces -- being able to improve quality of paper with sufficient balance, paper of fine quality finds out demonstrating the effectiveness which was excellent also in the newsprint from the first, and came to complete this invention.

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[0011] Otherwise as a cationic monomer, it is 2-hydroxy. - It is N, N, N, N', and N'-pentamethyl. - It is N'. - (3-(meta) acryloyl aminopropyl) -1, 3-propane dianmonium dichloride, 2-hydroxy-N-benzyl-N and N-diethyl - N' and N'-dimethyl - N' - (2-(meta) acryloyloxyethyl) -1, 3-propane dianmonium dibromide, N and N-dimethylaminoethyl (meta) acrylate, N, and N-dimethylaminopropyl (meta) AKURU amide, N-ethyl-N and N-dimethyl (2-(meta) acryloyloxyethyl) ammonium star's picture, N-benzyl-N and N-dimethyl-(3-(meta) acryloyl aminopropyl) ammoniumchloride, a diaryl amine, vinylpyridine, a vinyl imidazole, etc. are

mentioned.

[0012] The cross linking agent other than these monomers may be used. As a cross linking agent, the cross linking agent of the arbitration currently conventionally used for polyacrylamide system resin can be used. As an example, ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as propylene glycol (meta) acrylate and TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as hexa methylenebis (meta) acrylamide Epoxy acrylate, a divinylbenzene, urethane acrylate, diallyl phthalate, diallyl maleate, a triaryl SHIANU rate, triallyl isocyanurate, a dimethylolurea, a dimethylol ethylene urea, [0013] In addition, the poly aldehyde compounds, such as the poly methylol compounds, such as the Pori methylolurea, a methylol ethylene urea, a dimethylol glyoxal MONOU lane, dimethylol glyoxal diureine, uronic dimethylol, a dimethylol propylene urea, 1, 3-screw-(hydroxymethyl) tetrahydro-5-hydroxy-2-pyrimidinone, dimethylol triazon, the poly methylol melamine of a dimethylol melamine and others, and poly methylol ASETOGU Anacin, and glyoxal, glutaraldehyde, and dialdehyde starch, are mentioned.

[0014] The suitable polymerization initiator for the bottom of existence of ureas is used for the polymerization of the acrylamide system resin (A) of this invention, and it is 40-100 degrees C in temperature, and performs the reaction of 1 - 10 hours. The weight ratio of a urea and monomers is 80 - 50% of 20 - 50% pairs preferably 95 - 40% of 5 - 60% pairs. When there are more ureas than this range, or when few, the permeability to Kaminaka, surface reinforcement, internal reinforcement, a water resisting property, etc. cannot be balanced, and it is not desirable.

[0015] What has a well-known polymerization initiator is used. As a radical polymerization initiator, water-soluble catalysts, such as sodium persulfate, potassium persulfate, ammonium persulfate, a hydrogen peroxide, and the second cerium salt, are used 0.01 to 5% of the weight to total monomer weight. Moreover, redox polymerization can also be carried out using reducing agents, such as dimethylamine, a sodium hydrogensulfite, and sodium formaldehyde sulfoxylate. Moreover, a well-known chain transfer agent may be used if needed. As the class, allyl compounds, such as allyl alcohol, allylamine, and sodium allylsulfonate, mercaptoethanol, thioglycolic acid, its alkali-metal salt or ammonium salt, isopropyl alcohol, sodium hypophosphite, etc. are mentioned.

[0016] Acrylamides (a), alpha, beta partial saturation monocarboxylic acid, alpha, beta partial saturation dicarboxylic acid, The weight ratio of alpha, beta partial saturation tricarboxylic acid, a partial saturation sulfonic acid, and at least one sort of vinyl monomers (b) chosen from the group of those salts (a) is 99.5% - 50%, (b) is 0.5 - 50%, (a) is 98% - 85% preferably, and (b) is 2 - 15%.

[0017] As for the water soluble polymer mixed with acrylamide system resin (A), cellulotics, such as starch derivatives, such as starch, oxidization starch, and cation-ized starch, and a carboxymethyl cellulose, and polyvinyl alcohol are mentioned. the weight ratio of the water soluble polymer (B) mixed with the acrylamide system resin (A) containing ureas -- (A)/(B) -- 5 - 90%/-- they are 5 - 50% / 95 - 50% preferably 10 to 95%. According to the application of the target paper, the permeability to Kaminaka, surface reinforcement, internal reinforcement, and waterproof balance are considered, and a ratio is selected.

[0018] the front face of the paper of this invention -- quality of paper -- the surface coating liquid containing the constituent for improvement mixes the water solution of acrylamide system resin (A), and the water solution of the above-mentioned water soluble polymer (B), or it can cook after mixing the water solution of acrylamide system resin, and the dispersion liquid of the above-mentioned water soluble polymer, and it can adjust them. Additives, such as a surface sizing compound, a non-skid agent, antiseptics, a defoaming agent, a viscosity controlling agent, and a color, may be used together in the surface coating liquid of this invention. In addition, as for the concentration of coating liquid, it is desirable to be carried out at 0.1 - 15%.

[0019] The approach size press, a gate roll coater, a blade coating machine, or a calender performs the surface coating liquid in connection with this invention for carrying out coating to paper or the paper board is desirable. Moreover, coating can be carried out by the bar coating

machine, the knife coating machine, an air knife coater, etc. Moreover, coating of the surface coating liquid in connection with this invention can be carried out to various stencil paper, such as coat stencil paper (acid paper, alkaline paper), a newsprint, a liner, a coat ball, printing writing paper, a form form, a PPC form, inkjet printing paper, and a thermal paper. Although also whenever [ size / of stencil paper ] is arbitrary, when carrying out coating using size press etc., it is desirable to use an internal sizing compound in order to adjust the liquid adsorption of stencil paper.

[Translation done.]

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## EXAMPLE

[Example] Hereafter, although an example explains this invention, this invention is not restricted at all by these. In addition, measurement was performed according to the following approach. internal: on the strength -- SUKOTTO bond method; -- the internal bond tester (Kumagaya Riki Kogyo K.K. make) was used, and it measured on the bond strength of 1kg/cm<sup>2</sup>, and the conditions for 30 seconds.

surface: on the strength -- dry pick; RI printing testing-machine and nip width-of-face ink [ of 10mm ]; FINE INK. (the Dainippon Ink & Chemicals make --) ink for IGT printability trial T.V.= -- 18 or 20 -- wet -- a pick; RI printing testing machine -- nip width of face of 10mm mol ton roll use ink; -- CAPS G (Dainippon Ink & Chemicals make, for offset) ink T.V.= -- 8 or 10.5 -- the paper after printing all turned, the condition was observed with the naked eye, and five-step evaluation was performed by making 1 into \*\*, having made 5 as A.

wax pick; -- JIS P-8129 size whenever: -- Stockigt method; -- JIS P-8122-1976 [0021] In 11. 4 opening flask which attached the example agitator of manufacture, the thermometer, the ring current cooling pipe, and nitrogen gas installation tubing of acrylamide system resin (A), 402.32g of water, 90.89g (a urea is 40% of the weight of the sum total of a urea and a monomer) of ureas, 206.90g (97-mol %) of 50% acrylamide water solutions, 5.85g [ of itaconic acids ] (three-mol %) and 2-propanol 18.03g was taught, subsequently 6.85g of ammonium persulfate water solutions was added 5%, the temperature up was carried out to 80 degrees C under nitrogen gas installation, and it was made to react for 2 hours. 17.58g of ion exchange water was added to the obtained polymer, and the transparent water solution of the solid content of 29.8%, the viscosity of 5100cps, and pH7.10 was obtained. Let this be resin 1.

[0022] the coating liquid (12.7% of concentration and the viscosity in 50 degrees C are 30.5cps) which carried out 5.6 weight sections (solid content) mixing, and obtained the resin 1 of the above-mentioned example of manufacture in the oxidized starch 94.4 weight section (solid content) cooked at 12% of example 1 concentration -- acid paper of fine quality (basis-weight 75 g/m<sup>2</sup>) -- a system gate roll coater (a part for speed 800m/) -- coating -- it dried and coated paper was obtained. In addition, coating temperature was performed at 50 degrees C.

[0023] the coating liquid (13.1% of concentration and the viscosity in 50 degrees C are 33.5cps) which carried out 8.3 weight sections (solid content) mixing, and obtained the resin 1 of the above-mentioned example of manufacture in the oxidized starch 91.7 weight section (solid content) cooked at 12% of example 2 concentration -- the quality of an acid overlay (basis-weight 75 g/m<sup>2</sup>) -- a system gate roll coater (a part for 800m/) -- coating -- it dried and coated paper was obtained. In addition, coating temperature was performed at 50 degrees C.

[0024] the oxidized starch (the viscosity in 50 degrees C is 28.5cps) cooked at 12% of example concentration of a comparison -- acid paper of fine quality (the basis weight of 75g/m<sup>2</sup>) -- a system gate roll coater (a part for 800m/) -- coating -- it dried and coated paper was obtained. In addition, coating temperature was performed at 50 degrees C.

[0025] Paper durability was measured for the coated paper obtained by the evaluation example and the example of a comparison of the test paper after gas conditioning under the conditions of 20 degrees C and 65% relative humidity. In addition, measurement was performed according to the following approach. As the result was shown in Table 1, it was admitted that the direction of

the coated paper of an example was excellent in surface reinforcement, such as a wax pick, a dry pick, and a wet pick, the internal reinforcement as which it is indicated with SUKOTTO bond, and size nature. Moreover, it turns out that the coated paper of an example 2 excels the coated paper of an example 1 in dry pick, wet pick, and SUKOTTO bond and the Stockigt size.

[0026] Moreover, the osmosis condition of the starch to Kaminaka was measured using the coated paper by the example 1, the example 2, and the example of a comparison. Measurement exfoliated each coated paper in four layers, and carried out the quantum of the amount of starch of each class by the biosensor method (BF-DP:KS systems incorporated company) (as an amount of glucoses). This was shown in Table 1. Z shaft orientations of coated paper are expressed with % display in front Naka. That is, in 0% of Z shaft orientations, the rear face is expressed as the front face of coated paper, and 100% of Z shaft orientations, and it is shown [% / of Z shaft orientations / 25 ] that it is in 25% of location toward a rear face from the front face at the time of coating (surface approach).

[0027] The coated paper of an example can check a thing with many (starch has permeated) amounts of glucoses on each class of coated paper rather than the example of a comparison. When the paper Nakauchi section (25 – 65% of Z shaft orientations) compares especially, it is clear that many amounts of glucoses are contained in the example to the example of a comparison. Moreover, as for an example 1, the example 2 shows that there are also many amounts of glucoses of coated paper each class. Although the value of Table 2 is plotted to drawing 1, examples 1 and 2 can check that the glucose (oxidized starch) has permeated the interior of coated paper.

[0028]

[Table 1]

表 1 表面強度、内部強度及びサイズ性の測定結果

| 試 験 項 目          | 実施例 1 | 実施例 2 | 比 較 例 |
|------------------|-------|-------|-------|
| ワックスピック          | 18    | 18    | 14    |
| ドライピック           | 4.9   | 5.0   | 4.6   |
| ウェットピック          | 4.8   | 5.0   | 4.4   |
| スコットボンド [kgf/cm] | 2.03  | 2.09  | 1.90  |
| ステキヒトサイズ [sec]   | 76.6  | 78.1  | 74.4  |

[0029]

[Table 2]

表 2 塗工紙の各 Z 軸方向におけるグルコース量

|                      | グルコース量 (対紙重量%) |       |       |
|----------------------|----------------|-------|-------|
| Z 軸方向 (%)            | 実施例 1          | 実施例 2 | 比 較 例 |
| 12.4<br>13.2<br>13.5 | 2.05           | 2.21  | 1.75  |
| 27.6<br>33.1<br>43.0 | 0.44           | 0.52  | 0.00  |
| 39.8<br>59.6<br>63.0 | 0.70           | 0.83  | 0.05  |
| 82.7<br>84.1<br>89.3 | 2.43           | 2.67  | 1.26  |

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the amount of glucoses (weight for paper %), and the relation of Z shaft orientations (%) of paper.

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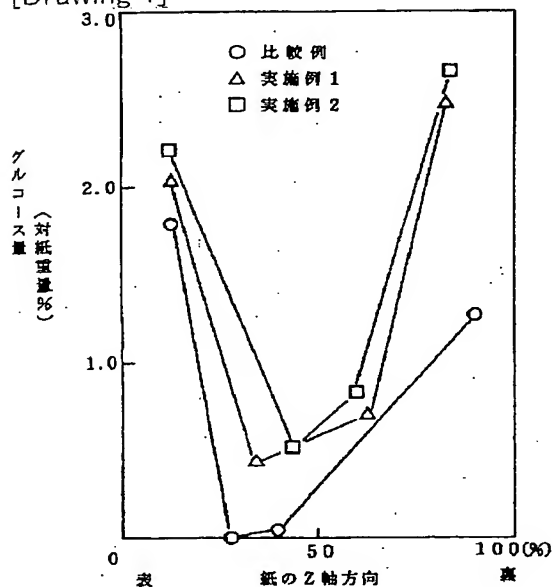
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## DRAWINGS

[Drawing 1]



[Translation done.]